

PCT

WORLD INTELLECTUAL PROPERTY ORGANIZATION  
International Bureau



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

<b>(51) International Patent Classification</b> <sup>5</sup> : C08L 77/00 // (C08L 77/00, 51:06)	A1	<b>(11) International Publication Number:</b> WO 94/13740 <b>(43) International Publication Date:</b> 23 June 1994 (23.06.94)
<b>(21) International Application Number:</b> PCT/CA93/00503 <b>(22) International Filing Date:</b> 24 November 1993 (24.11.93)  <b>(30) Priority Data:</b> 9225811.0 10 December 1992 (10.12.92) GB  <b>(71) Applicant:</b> DUPONT CANADA INC. [CA/CA]; P.O. Box 2200 Streetsville, Mississauga, Ontario L5M 2H3 (CA).  <b>(72) Inventors:</b> DOSHI, Shailesh, Ratilal; 1060 Redwood Crescent, Kingston, Ontario K7P 1Y9 (CA). BALTUS, Tom-Axel; 2163 Maplewood Drive, Burlington, Ontario L7R 2C7 (CA). McINTOSH, Margaret, Louise; 8 Bethnal Avenue, Etobicoke, Ontario M8Y 1Y6 (CA).  <b>(74) Agent:</b> GALLOWAY, Warren, J.; Sim & McBurney, 701 - 330 University Avenue, Toronto, Ontario M5G 1R7 (CA).		<b>(81) Designated States:</b> AU, CA, JP, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).  <b>Published</b> <i>With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>
<b>(54) Title:</b> EXTRUSION OR BLOW-MOULDING OF POLYAMIDE COMPOSITIONS  <b>(57) Abstract</b> <p>A blow moulding process in which a parison is formed from a polyamide composition and an extrusion process in which a profile is extruded from a polyamide composition are disclosed. The polyamide composition comprises (a) 55-90 % by weight of a polyamide selected from the group consisting of (i) polyamides having a weight average molecular weight of greater than 25 000, and (ii) polyamides that are soluble in formic acid and which have an RV measured in formic acid of at least 40; and (b) 10-45 % by weight of a polymer selected from the group consisting of grafted polymer and mixtures of grafted polymer and ungrafted polymer. Each of the grafted polymer and ungrafted polymer are independently selected from the polyolefins having a melt index of less than 10 dg/min. The polyolefin of the grafted polymer is grafted with 0.1-5.0 % by weight of an ethylenically unsaturated carboxylic acid or anhydride. The grafted polymer is 25-100 % by weight of the polymer of (b). The composition exhibits a relative increase in melt viscosity at low shear stress compared to the polyamide of (a). The compositions may be used in the blow moulding of for example bottles, containers and hollow under-the-hood automotive components and in the extrusion of for example rods, tubing, cable jacketing and other profiles.</p>		

*FOR THE PURPOSES OF INFORMATION ONLY*

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AT	Austria	GB	United Kingdom	MR	Mauritania
AU	Australia	GE	Georgia	MW	Malawi
BB	Barbados	GN	Guinea	NE	Niger
BE	Belgium	GR	Greece	NL	Netherlands
BF	Burkina Faso	HU	Hungary	NO	Norway
BG	Bulgaria	IE	Ireland	NZ	New Zealand
BJ	Benin	IT	Italy	PL	Poland
BR	Brazil	JP	Japan	PT	Portugal
BY	Belarus	KE	Kenya	RO	Romania
CA	Canada	KG	Kyrgyzstan	RU	Russian Federation
CF	Central African Republic	KP	Democratic People's Republic of Korea	SD	Sudan
CG	Congo	KR	Republic of Korea	SE	Sweden
CH	Switzerland	KZ	Kazakhstan	SI	Slovenia
CI	Côte d'Ivoire	LI	Liechtenstein	SK	Slovakia
CM	Cameroon	LK	Sri Lanka	SN	Senegal
CN	China	LU	Luxembourg	TD	Chad
CS	Czechoslovakia	LV	Latvia	TG	Togo
CZ	Czech Republic	MC	Monaco	TJ	Tajikistan
DE	Germany	MD	Republic of Moldova	TT	Trinidad and Tobago
DK	Denmark	MG	Madagascar	UA	Ukraine
ES	Spain	ML	Mali	US	United States of America
FI	Finland	MN	Mongolia	UZ	Uzbekistan
FR	France			VN	Viet Nam
GA	Gabon				

- 1 -

EXTRUSION OR BLOW-MOULDING OF POLYAMIDE COMPOSITIONS

5 The present invention relates to extrusion and  
blow-moulding processes using polyamide compositions and  
to such compositions, and especially to improvements  
therein. In particular, the invention relates to  
extrusion and blow-moulding processes in which the  
polyamide compositions have increased melt viscosity at  
low stress levels to impart melt sag resistance and  
10 moderately low viscosity at high stress levels, to impart  
improved extrudability.

Polyamides may be fabricated into a wide variety of  
products. The compositions used must have melt viscosity  
characteristics that are appropriate to the process being  
15 used, as discussed in published European patent  
application 0 295 906 of D.S. Dykes and K.D. Kuhnemann,  
published 1988 December 21. The use of compositions of  
polyamides and epoxides in extrusion processes is  
disclosed therein. Polyamide compositions for blow  
20 moulding are disclosed in U.S. Patent 5 122 570 of P.M.  
Subramanian, issued 1992 June 16, such compositions being  
semi-crystalline polyamide, selected toughening agent and  
an anhydride-rich ethylene copolymer.

Blow moulding and extrusion are important processing  
25 operations used in the manufacture of finished articles  
from polymeric compositions. Blow moulding is the  
process normally used for the manufacture of hollow  
articles for example bottles, jugs and the like, from  
thermoplastic polymers e.g. polyethylene, polypropylene  
30 and polyvinyl chloride. Blow moulding processes are  
finding increasing use in the manufacture of engineering  
and structural components, for example automotive under-  
the-hood components e.g. fluid reservoirs, resonators and  
the like, which have to be manufactured from so-called  
35 engineering polymers e.g. polyamides. Extrusion

- 2 -

processes are used for making continuous profiles for example pipe, tubing or other profiles of a specific cross-sectional shape. For automotive and other critical end-use applications, such extrusion processes utilize engineering polymers.

Both blow moulding and extrusion processes require polymer compositions with unique rheological characteristics for commercially acceptable operation. In blow moulding processes, molten polymer is extruded vertically from an annular die into a cavity between two halves of a mould, in the form of a tube known as a parison. The mould is then closed, capturing the parison between the halves of the mould. Air is blown into the parison to force the molten polymer into contact with and to the shape of the walls of the mould. The melt is cooled by circulation of a cooling fluid through channels within the walls of the mould, after which the moulded part is removed. During extrusion and until it is captured by the halves of the mould, the parison undergoes deformation characterized by extension or stretching of the parison under the influence of its own weight; as the only influence on the parison is its weight, the deformation occurs under low levels of stress. For successful operation of the process, the polymer must exhibit sufficiently high melt viscosity under low stress that the parison is able to support itself without extensive drawing, sagging or thinning in localized areas.

In an extrusion process, polymer melt is extruded from a die in the form of a continuous profile which then enters a cooling chamber for solidification. The travel of the extrudate from the die to the cooling chamber is usually free from any surface, and in order to preserve the desired cross-sectional shape the extrudate needs to be able to support itself without undergoing excessive

- 3 -

sagging. As with blow moulding processes, this also requires a polymer that has a sufficiently high melt viscosity under low levels of stress.

5 While high melt viscosity at low stress levels is required for the above processes, a moderately low melt viscosity is required under high levels of stress, and correspondingly high rates of flow, encountered in the extruder and die. A melt viscosity that is too high under these conditions leads to excessive pressure build-  
10 up and requires high torques for extrusion, which ultimately limits the rate of throughput obtainable from the extruder. Very high melt viscosity under these conditions may also lead to a phenomenon known as melt fracture where the surface of the extrudate becomes rough  
15 and wavy making the process difficult to operate and the resultant parts unacceptable.

The stress acting on a melt parison in a blow moulding process or on melt exudate during its travel from the die to the cooling chamber in an extrusion  
20 process is extensional in nature. However, it is extremely difficult to characterize melt viscosity of a polymer over a wide range of extensional stress, and melt viscosity measurements are commonly carried out over a wide range of shear stress.

25 Polyamides are characterized by low melt viscosity under both high and low shear stress i.e. they tend to have poor melt sag resistance. Techniques that increase the melt viscosity under low shear stress also tend to increase the melt viscosity under high shear stress, with  
30 the result that the resultant polyamide compositions tend to be unacceptable for blow moulding or extrusion processes. Preferred characteristics for blow moulding and extrusion are high viscosity at low shear stress and moderately low melt viscosity under high shear stress  
35 levels.

- 4 -

Polyamide compositions suitable for blow moulding and extrusion processes have now been found.

Accordingly, the present invention provides a blow moulding process in which a parison is formed from a polyamide composition, characterized in that said composition comprises:

(a) 55-90% by weight of a polyamide selected from the group consisting of (i) polyamides having a weight average molecular weight of greater than 25 000, and (ii) polyamides that are soluble in formic acid and which have an RV measured in formic acid of at least 40; and

(b) 10-45% by weight of a polymer selected from the group consisting of grafted polymer and mixtures of grafted polymer and ungrafted polymer, each of said grafted polymer and ungrafted polymer being independently selected from polyolefins having a melt index of less than 10 dg/min, the polyolefin of said grafted polymer having been grafted with 0.1-5.0% by weight of an ethylenically unsaturated carboxylic acid or anhydride, the grafted polymer being 25-100% by weight of the polymer of (b);

and said composition exhibiting a relative increase in melt viscosity at low shear stress compared to the polyamide of (a).

The present invention also provides an extrusion process in which a profile is extruded from a polyamide composition, characterized in that said composition comprises:

(a) 55-90% by weight of a polyamide selected from the group consisting of (i) polyamides having a weight average molecular weight of greater than 25 000, and (ii) polyamides that are soluble in formic acid and which have an RV measured in formic acid of at least 40; and

(b) 10-45% by weight of a polymer selected from the group consisting of grafted polymer and mixtures of

- 5 -

grafted polymer and ungrafted polymer, each of said grafted polymer and ungrafted polymer being independently selected from polyolefins having a melt index of less than 10 dg/min, the polyolefin of said grafted polymer having been grafted with 0.1-5.0% by weight of an ethylenically unsaturated carboxylic acid or anhydride, the grafted polymer being 25-100% by weight of the polymer of (b); and said composition exhibiting a relative increase in melt viscosity at low shear stress compared to the polyamide of (a).

In preferred embodiments of the processes of the invention, the polyamide has an amine end group content of at least 30 equivalents/ $10^6$  grams of polymer.

The present invention also provides a polyamide composition comprising:

(a) 55-90% by weight of a polyamide selected from the group consisting of (i) polyamides having a weight average molecular weight of greater than 25 000, and (ii) polyamides that are soluble in formic acid and which have an RV measured in formic acid of at least 40; and

(b) 10-45% by weight of a polymer selected from the group consisting of grafted polymer and mixtures of grafted polymer and ungrafted polymer, each of said grafted polymer and ungrafted polymer being independently selected from polyolefins having a melt index of less than 10 dg/min, the polyolefin of said grafted polymer having been grafted with 0.1-5.0% by weight of an ethylenically unsaturated carboxylic acid or anhydride, the grafted polymer being 25-100% by weight of the polymer of (b); and said composition exhibiting a relative increase in melt viscosity at low shear stress compared to the polyamide of (a).

In a preferred embodiment of the composition of the

- 6 -

invention, the polyamide has an amine end group content of at least 30 equivalents/10<sup>6</sup> grams of polymer.

In the drawing, Fig. 1 illustrates melt viscosity-shear stress data for a number of compositions of Example I.

The invention relates to polyamide compositions and their use in certain processes viz. blow moulding and extrusion processes. The polyamide is a condensation polymer, commonly known as "nylon", having recurring units of aliphatic and/or aromatic amide groups in the molecular chain. Examples of aliphatic polyamides are nylon 6, nylon 66, nylon 610, nylon 612, and their related copolymers e.g. nylon 6/66. Aromatic polyamides may be formed from aromatic acids e.g. terephthalic and/or isophthalic acids, especially in which the diamine is hexamethylene diamine, 2-methyl pentamethylene diamine, dodecamethylene diamine and/or other related branched and unbranched diamines. The polyamide forms 55-90% by weight of the composition, especially 60-85% of the composition.

In one embodiment of the invention, the polyamides used in the composition have a weight average molecular weight of greater than 25 000. Polyamides with a weight average molecular weight of less than 25 000 generally will not exhibit an acceptable melt viscosity at low shear rates. Preferably, the weight average molecular weight is less than 100 000, especially less than 50 000 for acceptable melt viscosity under high shear i.e. during extrusion.

In another embodiment, the polyamides are soluble in formic acid, and the molecular weight of the polymers may be characterized in terms of relative viscosity (RV), which is defined as the ratio of the viscosity of an 8.4% solution of the polymer (by weight) in 90% formic acid solvent to the viscosity of the formic acid solvent at



- 7 -

room temperature. In this embodiment, the polyamides used in the compositions have an RV of at least about 40; such polymers are commercially available e.g. as injection moulding grade nylon polymers. Polymers with an RV of less than 40 will generally not exhibit an acceptable melt viscosity at low shear rates. The RV should be less than 200, preferably less than 100, for acceptable melt viscosity under high shear e.g. during extrusion.

The polyamide preferably has an amine end group content of at least 30 equivalents/ $10^6$  grams of polymer, especially at least 35 equivalents/ $10^6$  grams of polymer, for acceptable compatibilization of the polyamide and polyolefin phases of the composition by the acid or anhydride-grafted polymers. At lower amine end group contents, the compatibilization of the nylon and polyolefin phases may be inadequate; this can manifest itself as, for example, insufficient enhancement of low shear viscosity or poor pinch-off strength in the blow moulded parts. Poor pinch-off strength occurs when two parts e.g. the two halves, of a finished blow moulded article are not bonded together with adequate strength, and the two halves may be readily pulled apart.

The polyolefins used in the present invention may be polyethylene, polypropylene, copolymers of two or more of ethylene, propylene, butene, hexene, octene, butadiene, hexadiene and related monomers, or olefinic thermoplastic elastomers. The polyolefins preferably have a low melt index i.e. a high melt viscosity; melt index is measured by the procedure of ASTM D-1238, at temperatures appropriate to the particular polymer. The melt index of the polyolefin should be less than about 10 dg/min, preferably less than about 2 dg/min. It is preferred to use a polyolefin with a density of less than about 0.94 g/cm<sup>3</sup>, especially less than about 0.935 g/cm<sup>3</sup>, to improve

- 8 -

modification of the rheology of the composition and increase toughness of the fabricated articles. In especially preferred embodiments, at least part of the polyolefin is a low modulus elastomeric polymer e.g. ethylene/propylene/diene (EPDM) thermoplastic elastomer, to improve modification of the rheology of the composition and increase toughness.

The compatibilization between the nylon and polyolefin phases is achieved by the use of functionalized or grafted polymers that are reactive and/or comparative with both the nylon and polyolefin phases. The grafted polymers are polyolefins, as defined above, that have been grafted with acid and/or anhydride group-containing monomers. Examples of the acids and anhydrides, which may be mono-, di or polycarboxylic acids, are acrylic acid, methacrylic acid, maleic acid, fumaric acid, itaconic acid, crotonic acid, itaconic anhydride, maleic anhydride, and substituted maleic anhydride e.g. dimethyl maleic anhydride or citraconic anhydride, nadic anhydride, nadic methyl anhydride and tetrahydric phthalic anhydride. Examples of the derivatives of the unsaturated acids are salts, amides, imides and esters e.g. mono- and disodium maleate, acrylamide, maleimide, glycidyl methacrylate and diethyl fumarate. The preferred grafting monomer is maleic anhydride. Such polymers should also have high viscosity, as characterized by low melt index which has to be measured at a temperature appropriate to the particular polymer. A melt index of less than about 10 dg/min is acceptable for the grafted polyolefins, with melt indices of less than 2 dg/min being preferred. The acid and/or anhydride graft level should be in the range of about 0.1%-5%, especially 0.3-4%, by weight. A method for the grafting of ethylenically unsaturated carboxylic acids or anhydrides onto polyolefins is described in U.S.

- 9 -

Patent 4 612 155 of R.A. Zelonka and C.S. Wong, issued 1986 September 16. It is preferred to use grafted polymer with a density of less than  $0.94 \text{ g/cm}^3$ , especially less than about  $0.935 \text{ g/cm}^3$ , to improve modification of the rheology of the composition and increase toughness of the fabricated article. It is especially preferred that at least part of the grafted polymer is a grafted low modulus elastomeric polymer e.g. ethylene-propylene-diene (EPDM) thermoplastic elastomer grafted with acid and/or anhydride group-containing monomers, to improve modification of the rheology of the composition and to increase toughness.

The polyolefins and grafted polymer are used in amount such that the ratio is in the range of about 0:1 to 3:1, by weight, especially 0.2 to 2.5:1.[start]

Fillers and reinforcements used for improving physical mechanical properties of thermoplastic polymers may also be incorporated into the compositions. Examples of such reinforcements and fillers are glass fibres, glass flakes, glass spheres, particulate minerals e.g. calcium carbonate, talc, mica, wollastonite, clay, silica and the like, minerals synthetic fibres e.g. calcium sulphate fibres, aramid fibres etc. The fillers and reinforcements, generally tend to increase the melt viscosity at low shear rates to higher values than for the equivalent unfilled or unreinforced compositions, and thus provide even greater resistance to melt sagging.[end]

The compositions may be prepared using conventional apparatus for the mixing and blending of polymer compositions, examples of which are single and multiple screw extruders, internal batch and continuous mixers, roll mills, kneaders and the like. Alternatively, the compositions may be prepared by dry mixing the components together, and melt fabricating the resulting mixtures

- 10 -

directly into articles using blow moulding or extrusion processes.

5 The compositions may be used in blow moulding and extrusion processes e.g. in the manufacture of bottles, containers, hollow under-the-hood automotive components and other blow moulded articles, and in the manufacture of rods, tubing, cable jackets and other extruded profiles.

10 The invention is illustrated by the following examples.

Example I

The shear rate - melt viscosity curves were determined for the polymer compositions listed below, at temperatures appropriate to the polymers in the compositions and using a Kayness capillary viscometer. Further details and the shear rate-melt viscosity data are tabulated in Table I.

The composition were:

20 Composition (a) is a comparative composition that is an injection moulding grade nylon 6 having a relative viscosity (RV) of 51;  
Composition (b) is a comparative composition that is an injection moulding grade nylon 66 having an RV of 52;  
25 Composition (c) is a comparative composition that is an extrusion grade nylon 6 with an RV of 140;  
Composition (d) is a comparative composition that is an extrusion grade nylon 6 with an RV of 253;  
Composition (e) is a comparative composition that is an extrusion grade nylon 6 with an RV of 285;  
30 Composition (f) is a blend, on a weight basis, of (i) 59.75% Nylon 66 having an RV of 52 and an amine end level of 55 equivalent/10<sup>6</sup> gm, (ii) 25% polyethylene having a melt index of 0.6 dg/min and a density of 0.919 g/cm<sup>3</sup>, (iii) 15% of a grafted polyethylene having a melt index  
35 of about 2 dg/min, a density of 0.92 g/cm<sup>3</sup> and containing

- 11 -

approximately 1% grafted maleic anhydride, and (iv) 0.25% of thermal stabilizers;

Composition (g) is a blend, on a weight basis, of (i) 59.75% nylon 6 having an RV of 46 and amine end level of 23 equivalents/ $10^6$  gm, (ii) 25% polyethylene having a melt index of 1.4 dg/min and a density of  $0.92 \text{ g/cm}^3$ , (iii) 10% grafted polyethylene having a melt index of about 2 dg/min, a density of  $0.92 \text{ g/cm}^3$  and containing approximately 1% grafted maleic anhydride, (iv) 5% grafted ethylene-propylene-diene thermoplastic elastomer containing approximately 1.7% grafted fumaric acid, and (v) 0.25% of thermal stabilizers;

Composition (h) is a blend, on a weight basis, of (i) 69.75% nylon 6 having an RV of 48 and amine end level of 37 equivalents/ $10^6$  gm, (ii) 13% polyethylene having a melt index of 1.4 dg/min and a density of  $0.92 \text{ g/cm}^3$ , (iii) 6.5% grafted polyethylene with a melt index of about 2 dg/min, a density of about  $0.92 \text{ g/cm}^3$  and containing approximately 1% grafted maleic anhydride, (iv) 6.5% grafted ethylene-propylene-diene thermoplastic elastomer containing approximately 1.7% grafted fumaric acid, (v) 4.4% black pigment concentrate, and (vi) 0.25% of thermal stabilizers;

Composition (i) is a blend, on a weight basis, of (i) 69.75% nylon 6 having an RV of 67 and amine end level of 51 equivalents/ $10^6$  gm, (ii) 13% polyethylene with a melt index of 1.4 dg/min and a density of  $0.92 \text{ g/cm}^3$ , (iii) 6.5% grafted polyethylene with a melt index of about 2 dg/min, a density of about  $0.92 \text{ g/cm}^3$  and containing approximately 1% grafted maleic anhydride, (iv) 6.5% grafted ethylene-propylene-diene thermoplastic elastomer with approximately 1.7% grafted fumaric acid, (v) 4.4% black pigment concentrate, and (vi) 0.25% of thermal stabilizers;

- 12 -

Composition (j) is a blend, on a weight basis, of (i) 69.75% nylon 6 having an RV of 140 and amine end level of 36 equivalents/10<sup>6</sup> gm, (ii) 13% polyethylene having a melt index of 1.4 dg/min and a density of 0.92 g/cm<sup>3</sup>, (iii) 5 6.5% grafted polyethylene having a melt index of about 2 dg/min, a density of about 0.92 g/cm<sup>3</sup> and containing approximately 1% grafted maleic anhydride, (iv) 6.5% grafted ethylene-propylene-diene thermoplastic elastomer having approximately 1.7% grafted fumaric acid, (v) 4.4% 10 black pigment concentrate, and (vi) 0.25% of thermal stabilizers;

Composition (k) is a blend, on a weight basis, of (i) 69.75% nylon 6 having an RV of 78 and amine end level of 14 equivalents/10<sup>6</sup> gm, (ii) 13% polyethylene having a melt 15 index of 1.4 dg/min and a density of 0.92 g/cm<sup>3</sup>, (iii) 6.5% grafted polyethylene having a melt index of about 2 dg/min, a density of about 0.92 g/cm<sup>3</sup> and containing approximately 1% grafted maleic anhydride, (iv) 6.5% grafted ethylene-propylene-diene thermoplastic elastomer 20 with approximately 1.7% grafted fumaric acid, (v) 4.4% black pigment concentrate, and (vi) 0.25% of thermal stabilizers; and

Composition (l) is a blend, on a weight basis, of (i) 69.75% nylon 6 having an RV an amine end level of 23 25 equivalents/10<sup>6</sup> gm, (ii) 13% polyethylene having a melt index of 1.4 dg/min and a density of 0.92 g/cm<sup>3</sup>, (iii) 6.5% grafted polyethylene having a melt index of about 2 dg/min, a density of about 0.92 g/cm<sup>3</sup> and containing approximately 1% grafted maleic anhydride, (iv) 6.5% 30 grafted ethylene-propylene-diene thermoplastic elastomer having approximately 1.7% grafted fumaric acid, (v) 4.4% black pigment concentrate, and (vi) 0.25% thermal stabilizers.

In the above compositions, the polyethylene was an

- 13 -

ethylene/butene-1 copolymer containing 6.7% butene-1. The same type of polymer was used for the grafted polymer. The EPDM elastomer contained 70% by weight of ethylene, 26% by weight of propylene and 4% by weight of hexadiene.

The above compositions were prepared by dry mixing the components of the composition, and then melt blending the resultant mixture in a Werner & Pfleiderer 53 mm twin screw extruder at 250 rpm. For compositions based on nylon 6, a temperature profile of 210°C in the feed section, 230-235°C in the barrel section and 235°C at the die was used. For compositions based on nylon 66, a temperature profile of 240°C in the feed section, 270-280°C in the barrel section and 280°C at the die was used. The resulting polymer melt was pelletized to obtain the composition in the form of pellets.

Compositions were evaluated in blow moulding and extrusion processes. Blow moulding evaluation was carried out using a blow moulding apparatus with an accumulator head of 1.4 kg capacity and a representative mould for an automotive plenum chamber. Extrusion evaluation was carried out by making nominally 6 mm diameter tubing. A melt temperature of about 228°C was used for nylon 6 compositions, and a melt temperature of about 265°C was used for nylon 66 compositions.

Compositions (a) and (b) are comparative examples of low RV nylon 6 and nylon 66 compositions that are intended for use in injection moulding apparatus. The melt viscosities are extremely low, compared with compositions required for blow moulding and extrusion. Thus, these compositions are unsuitable for blow moulding and extrusion process.

Compositions (c), (d) and (e) are comparative examples of nylon 6 compositions having higher RV values than Compositions (a) and (b), and were evaluated in blow

- 14 -

5 moulding processes. Compositions (c) and (d) were difficult to blow mould because the melt viscosities of these compositions at low levels of stress were not sufficiently high to prevent excessive sagging of the melt parison. Compositions (e) exhibited extremely high melt viscosity, which made the composition difficult to extrude into a parison at acceptable rates; however, the parison exhibited excellent resistance to sagging under its own weight.

10 Compositions (f), (g), (h) and (i) illustrate the present invention. Compositions (f) and (g) were evaluated in small diameter tubing extrusion process. Both compositions were processed successfully into tubing with nominal diameter of about 6 mm.

15 Compositions (h) and (i) were evaluated in the blow moulding operation, and compared against high RV nylon 6 compositions (c), (d) and (e). In a blow moulding operation involving the same size of parison, the stress acting on the parison due to the weight of the parison will be the same for all compositions, thereby providing a comparison at common levels of stress.

20 In a blow moulding process, Compositions (h) and (i) exhibited excellent resistance to melt sagging, and yet were easy to extrude at high throughput. It took less than half the time to extrude sufficient melt to make the blow moulded parts, as compared with the time required for Composition (e). Composition (i) exhibited even greater resistance to sagging than (h), due to the higher RV of the nylon 6 composition.

25 Composition (j) is similar to Composition (h), except that it is based on nylon 6 with a substantially higher RV. This composition exhibited extremely high melt viscosity at high shear stress, and was extremely difficult to extrude into parisons.

30 Composition (i) is also similar to Composition (h),



- 15 -

except that it is based on nylon 6 with higher RV but a lower level of amine ends. Blow moulding evaluation of this composition showed that although it has sufficiently high viscosity at low stress levels to exhibit good resistance to melt parison sagging, it lacked so-called pinch-off strength, which is defined as the stress necessary to pull apart two halves of the moulded article bonded by pinch-off in the mould cavity, after the article has been moulded.

Composition (l) is similar to (h), being based on nylon 6 with a low level of amine ends. While it is possible to blow mould this composition, its resistance to sagging of the parison was not as great as that of either of Compositions (h) or (i).

Figure 1 illustrates melt viscosity - shear stress relationships for Compositions (c), (d), (e), (h) and (i). In the case of the high RV nylon 6 compositions (c), (d) and (e), the melt viscosity curve flattens out towards the low shear stress end, and the viscosity does not show a rapid rise as the shear stress is reduced; consequently, any attempt to increase the melt viscosity at low stress by increasing the molecular weight i.e. increasing RV, also increases the melt viscosity under high shear stress levels thereby making the composition difficult to extrude. In contrast, Compositions (h) and (i) exhibit a completely different behaviour, characterized by a steep viscosity curve with the melt viscosity rising sharply as the shear stress is reduced. Such high viscosity at low shear stress levels provides excellent resistance to melt sagging or drawing of the parison during a blow moulding operation. On the other hand, the melt viscosity drops to low values at high shear stress, below that of Compositions (c), (d) or (e), which allows for relatively easy extrusion of material. Thus, the present invention provides a way of modifying

- 16 -

rheology of relatively low molecular weight polyamides such that the resistance to melt sagging is improved without comprising the ease of extrusion.

5

TABLE I

## Shear Rate - Viscosity Relationships

Comp. Temp. &lt;-----Shear Rate (1/s)-----&gt;

(°C)	0.087	0.174	0.26	0.347	0.52	1	2
(a) 240							
(c) 240					4270	3440	3420
(d) 240					13470	10110	10720
(e)* 240	36830	31890	30090	29640	26570	19310	
(f) 280							
(g) 240							
(h) 240	35030	23130	18260	15380	12870	8910	6890
(i) 240	53890	35920	33080	29420	24100	16020	
(j) 240							
(k) 240							
(l) 240							

10

15

20

## Shear Rate - Viscosity Relationships (cont.)

Comp. Temp. &lt;-----Shear Rate (1/s)-----&gt;

(°C)	10	30	50	100	250	300	500	1000
(a) 240	480	460		390		340		210
(c) 240	3340	2220	2190	1720	1140	1080	710	490
(d) 240	6570		3720	2560	1570		1080	
(e) 240	9220		4370	3020	1440		990	M.F.**
(f) 280	3000	1600		850		450		240
(g) 240	2540		1380	1010	610		410	280
(h) 240	4180		2110	1520	970		650	
(i) 240	6430	3700	2840	1930		1130		430
(j) 240	8510	4920		2420		M.F.**		M.F.**
(k) 240	3080	1900		1130		650		340
(l) 240	2380	1520		970		570		290

25

30

35

- 17 -

## Shear Rate - Viscosity Relationships (cont.)

Comp. Temp. &lt;-----Shear Rate (1/s)-----&gt;

(°C)	25	100	350	830	1200	
(b)	280	250	270	230	190	170

5

Note: Data for Composition (e) is representative data, as melt viscosity data was changing during measurement.

MF = melt fracture occurred.

10

Viscosity is reported in Pa.s

The samples of the compositions were dried at 80°C for two hours in a dehumidified drier to moisture levels below 0.05% by weight prior to measurements being conducted.

15

The data represent apparent viscosity and shear stress; Bagley and Robinowitch corrections were not applied.

Example II

Short glass fibre reinforced compositions were prepared by melt blending and uniformly dispersing various levels of short glass fibres into Composition (h) of Example I. On a weight basis, these compositions were nominally as follows:

25	Composition (m)	87% Composition (h) of Example 1	13% short glass fibres
	Composition (n)	80% Composition (h) of Example 1	20% short glass fibres
30	Composition (o)	75% Composition (h) of Example 1	25% short glass fibres
35	Composition (p)	70% Composition (h) of Example 1	30% short glass fibres

The melt blending and glass dispersion was carried out in a 53 mm Werner and Pfleiderer twin screw extruder running at 200 rpm using a temperature profile of 210°C in the feed section, 230-235°C in the barrel section and

- 18 -

235°C at the die. In each case, the resulting melt was pelletized to obtain the composition in the form of pellets.

5 The shear rate-viscosity relationships for these compositions were determined using a Kayness capillary viscometer at 240°C. The data are tabulated in Table II.

TABLE II

Shear Rate - Viscosity Relationships								
10	Comp.	-----Shear Rate (1/s)----->						
		0.52	1	2	10	50	100	250 500
	(m)	51000	29000	1900	8400	3400	2200	1200 740
	(n)	70000	40000	26000	10600	3900	2500	1400 900
	(o)	61000	35000	23000	9900	3700	2400	1400 940
15	(p)	63000	37000	21000	10500	3700	2400	1400 900

Viscosity is reported in units of Pa.s

20 The samples of the compositions were dried at 80°C for two hours in a dehumidified drier to moisture levels below 0.05% by weight prior to measurements being conducted.

The data represent apparent viscosity and shear stress; Bagley and Robinowitch corrections were not applied.

25 Compositions were evaluated in the blow moulding process of Example I. The mould used was designed to produce hollow rectangular plaques measuring roughly 42 x 10 x 5 cm. It had inserts to produce either textured sections or two square draw pockets measuring  
30 approximately 3.8 x 3.8 x 0.6 cm and 1.9 x 1.9 x 0.6 cm on one side of the blow moulded parts. The draw pockets provide a measure of the ability of the composition to be drawn into features representing sharp changes in geometry. A melt temperature of about 235°C was used for  
35 blow moulding evaluation of all of the compositions.

- 19 -

5 All of the compositions exhibited excellent  
resistance to melt sagging. Compared to the unreinforced  
composition (h) of Example 1, the above composition  
exhibited significantly lower die swell in the thickness  
and diameter of the parison. All the compositions were  
able to produce good blow moulded parts when the textured  
insert was used in the mould. When the insert with  
square draw pockets was used, compositions (m) and (n)  
produced good parts. In case of compositions (o) and  
10 (p), the draw pockets were not sharply defined and had  
thin rounded corners. This indicates a reduced  
drawability of the melt at higher glass loadings.

15

20

25

30

35

- 20 -

CLAIMS:

1. A blow moulding process in which a parison is formed from a polyamide composition, characterized in that said composition comprises:

(a) 55-90% by weight of a polyamide selected from the group consisting of (i) polyamides having a weight average molecular weight of greater than 25 000, and (ii) polyamides that are soluble in formic acid and which have an RV measured in formic acid of at least 40; and

(b) 10-45% by weight of a polymer selected from the group consisting of grafted polymer and mixtures of grafted polymer and ungrafted polymer, each of said grafted polymer and ungrafted polymer being independently selected from the polyolefins having a melt index of less than 10 dg/min, the polyolefin of said grafted polymer having been grafted with 0.1-5.0% by weight of an ethylenically unsaturated carboxylic acid or anhydride, the grafted polymer being 25-100% by weight of the polymer of (b); and said composition exhibiting a relative increase in melt viscosity at low shear stress compared to the polyamide of (a).

2. An extrusion process in which a profile is extruded from a polyamide composition, characterized in that said composition comprises:

(a) 55-90% by weight of a polyamide selected from the group consisting of (i) polyamides having a weight average molecular weight of greater than 25 000, and (ii) polyamides that are soluble in formic acid and which have an RV measured in formic acid of at least 40; and

(b) 10-45% by weight of polymer selected from the group consisting of grafted polymer and mixtures of grafted polymer and ungrafted polymer, each of said grafted polymer and ungrafted polymer being independently

- 21 -

selected from polyolefins having a melt index of less than 10 dg/min, the polyolefin of said grafted polymer having been grafted with 0.1-5.0% by weight of an ethylenically unsaturated carboxylic acid or anhydride, the grafted polymer being 25-100% by weight of the polymer of (b); and said composition exhibiting a relative increase in melt viscosity at low shear stress compared to the polyamide of (a).

3. The process of Claim 1 or Claim 2 in which the polyamide has an amine end group content of at least 30 equivalents/ $10^6$  grams of polymer.

4. The process of any one of Claims 1-3 in which the weight average molecular weight of any polyamide of (a)(i) is less than 100 000 and the RV of any polyamide of (a)(ii) is less than 200.

5. The process of any one of Claims 1-4 in which the polyamide is a polyamide of (a)(i).

6. The process of any one of Claims 1-4 in which the polyamide is a polyamide of (a)(ii).

7. The process of any one of Claims 1-6 in which the polyamide is an aliphatic polyamide.

8. The process of any one of Claims 1-7 in which the polyolefin is grafted with maleic anhydride.

9. A polyamide composition comprising:

(a) 55-90% by weight of a polyamide selected from the group consisting of (i) polyamides having a weight average molecular weight of greater than 25 000, and (ii) polyamides that are soluble in formic acid and which have an RV measured in formic acid of at least 40; and

(b) 10-45% by weight of a polymer selected from the group consisting of grafted polymer and mixtures of grafted polymer and ungrafted polymer, each of said grafted polymer and ungrafted polymer being independently selected from polyolefins having a melt index of less

- 22 -

than 10 dg/min, the polyolefin of said grafted polymer having been grafted with 0.1-5.0% by weight of an ethylenically unsaturated carboxylic acid or anhydride, the grafted polymer being 25-100% by weight of the polymer of (b); and said composition exhibiting a relative increase in melt viscosity at low shear stress compared to the polyamide of (a).

10. The composition of Claim 9 in which the polyamide has an amine end group content of at least 30 equivalents/ $10^6$  grams of polymer.

11. The compositions of Claim 9 or Claim 10 in which the weight average molecular weight of any polyamide of (a)(i) is less than 100 000 and the RV of any polyamide of (a)(ii) is less than 200.

12. The composition of any one of Claims 9-11 in which the polyamide is a polyamide of (a)(i).

13. The composition of any one of Claims 9-11 in which the polyamide is a polyamide of (a)(ii).

14. The composition of any one of Claims 9-13 in which the polyolefin is grafted with maleic anhydride.



1/1

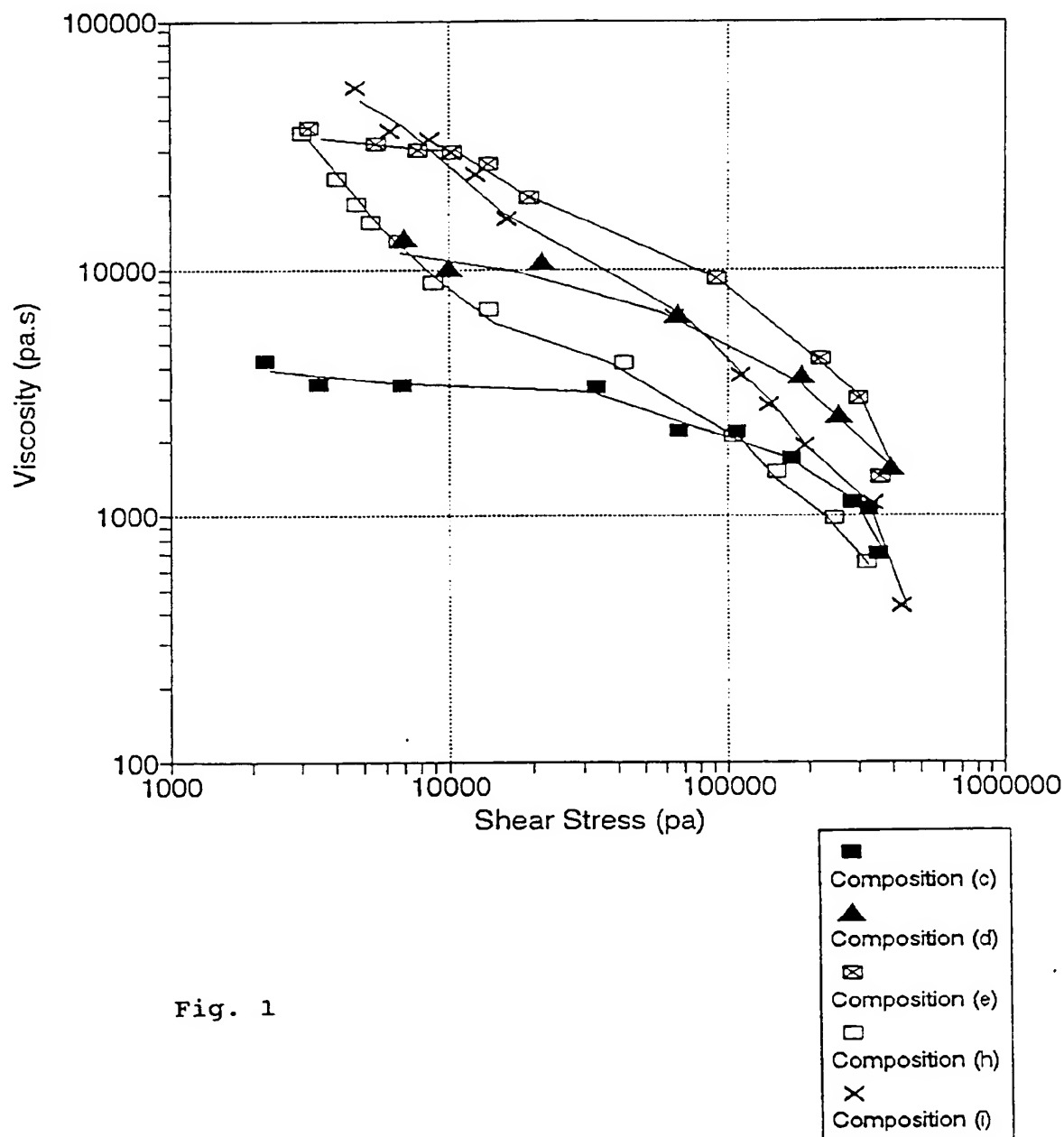


Fig. 1

SUBSTITUTE SHEET

## INTERNATIONAL SEARCH REPORT

International Application No.  
PCT/CA 93/00503

A. CLASSIFICATION OF SUBJECT MATTER  
IPC 5 C08L77/00 //(C08L77/00, 51:06)

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 5 C08L

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	EP,A,0 235 876 (TONEN SEKIYU) 9 September 1987 see the whole document ---	1
Y	PATENT ABSTRACTS OF JAPAN vol. 010, no. 023 (C-325) 29 January 1986 & JP,A,60 177 073 (MITSUBISHI KASEI KOGYO KK) 11 September 1985 see abstract ---	1
Y	PATENT ABSTRACTS OF JAPAN vol. 009, no. 104 (C-279) 8 May 1985 & JP,A,59 232 135 (SHOWA DENKO KK) 26 December 1984 see abstract ---	1
Y	EP,A,0 469 693 (BUNA AG) 5 February 1992 see the whole document ---	1
-/--		

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

## \* Special categories of cited documents :

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier document but published on or after the international filing date
- "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

- "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- "&" document member of the same patent family

Date of the actual completion of the international search

19 April 1994

Date of mailing of the international search report

06.05.94

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2  
NL - 2280 HV Rijswijk  
Tel. (+ 31-70) 340-2040, Tx. 31 651 epo nl,  
Fax (+ 31-70) 340-3016

Authorized officer

Leroy, A

## INTERNATIONAL SEARCH REPORT

International Application No

PCT/CA 93/00503

## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	EP,A,0 337 153 (ASHLAND OIL) 18 October 1989 see claims; examples 1-3 ---	1
A	GB,A,2 194 540 (EMS-INVENTA) 9 March 1988 ---	
A	EP,A,0 372 866 (DU PONT CANADA) 1 December 1989 -----	

Form PCT/ISA/210 (continuation of second sheet) (July 1992)

# INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/CA 93/00503

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP-A-0235876	09-09-87	JP-A- 62158740	14-07-87
		JP-B- 5005259	21-01-93
		JP-A- 62158739	14-07-87
		JP-A- 62223250	01-10-87
		JP-B- 5008939	03-02-93
		JP-A- 62223251	01-10-87
		DE-A- 3785472	27-05-93
EP-A-0469693	05-02-92	DE-A- 4123963	21-01-93
EP-A-0337153	18-10-89	US-A- 4814379	21-03-89
		DE-D- 68909085	21-10-93
		JP-A- 1311149	15-12-89
GB-A-2194540	09-03-88	CH-A- 671022	31-07-89
		DE-A,C 3728334	03-03-88
		FR-A- 2603293	04-03-88
		FR-A- 2635329	16-02-90
		GB-A- 2218105	08-11-89
		JP-A- 6041296	15-02-94
		JP-A- 63061040	17-03-88
EP-A-0372866	13-06-90	GB-A- 2225582	06-06-90
		AU-B- 621956	26-03-92
		AU-A- 4535689	07-06-90
		JP-A- 2194077	31-07-90